

FLASH PYROLYSIS OF COAL IN NONREACTIVE GASES

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ABSTRACT

Coal pyrolysis experiments were carried out with a New Mexico subbituminous coal in the presence of nonreactive He, N₂, and Ar gases in an entrained downflow tubular reactor. The percent carbon conversions to CH₄, C₂H₄, BTX, CO and CO₂ were determined as a function of temperature and residence time at 50 psi. In helium atmosphere, the yields of methane and CO_x reached asymptotic values in about 1 sec and ethylene was produced throughout the length of the BNL reactor corresponding to a coal particle residence time of 1.7 sec. The relative yields of individual products were influenced by the pyrolysis atmosphere but the total carbon conversion remained almost unaffected. A reduction in the cationic content of coal by acid treatment enhanced the production of CO and CO₂ but inhibited the formation of ethylene.

INTRODUCTION

Devolatilization plays an important role in the conversion of coal to gases and liquids. It is generally agreed that combustion and gasification of coal is preceded by the release of volatile matter from the coal particle. Under rapid heating conditions ($>10^4$ °K/sec), volatile yields in excess of those from proximate analysis ($<10^2$ °K/sec) have been obtained (Budzioch, 1970). Other reaction parameters which affect the volatile yields during pyrolysis of coal are: reaction temperature, particle residence time, and gas pressure. In addition, the pyrolysis product composition also depends on the nature of the entraining gas medium.

Previous research at Brookhaven mainly focused on the yields, distribution, and kinetics of formation of products in reactive hydrogen and methane atmospheres (Sundaram, 1982; Steinberg, 1982; Sundaram, 1984). An investigation was, therefore, initiated with special emphasis on determination of flash pyrolytic behavior of coal in nonreactive gases and their mixtures. This paper is specifically concerned with the effect of gaseous atmosphere on the pyrolysis product yields.

EXPERIMENTAL

Figure 1 presents the schematics of the entrained downflow isothermal tubular reactor. A detailed description of the design, construction, and operation of the reactor is available (Sundaram, 1982). The reactor is heated electrically by four clamshell-type heaters and designed for operation at temperatures up to 1050°C and pressures up to 4000 psig. Particle heatup rates in the range 10^4 to 10^5 °K/sec are attainable in this reactor. Other carbonaceous materials such as biomass and oil shale have also been successfully run in the unit.

Coal (<150 μm in diameter) is mixed with 10 to 30% by weight of Cab-O-Sil, an inert fumed silica powder, to prevent agglomeration, and is fed by gravity into the preheated gas stream at an average flow rate of about 400 to 600 g/hr. The preheated gas is injected at an average volumetric flow rate of about 40 to 45 l/min. At the beginning of the run, the coal and gas flow rates are so adjusted that a constant solid-to-gas feed ratio of 0.15 to 0.25 g coal/l gas is maintained in order to be able to continue a dilute phase operation. The residence time of the coal particles is determined from the free-fall velocity of the solid particles using Stoke's law and from the velocity of the entraining gas molecules.

The proximate and ultimate analyses of coal used in the study are shown in Table 1. The acid-washed New Mexico subbituminous coal was prepared by treating the original coal with large excess of 1 N HCl at room temperature followed by washing with deionized water until the filtrate was free of chloride ions. All coal samples were dried in a vacuum oven for at least 24 hours before feeding into the reactor. The gases used were of 99% or higher purity. The density, heat capacity, and thermal conductivity data for experimental gases are listed in Table 2. 50-50 gas mixtures of helium and argon were prepared from pure gases on a volume percent basis.

The principal pyrolysis products were methane, ethylene, BTX, CO, and CO₂. Product gas samples, corresponding to coal particle residence times variable up to 2 sec, are taken from any of the four sample taps located at 2-ft intervals throughout the length of the reactor and analyzed via on-line GC. Products heavier than BTX are formed only at low temperatures ($<800^\circ\text{C}$) and collected in water-cooled condensers during isothermal runs and analyzed separately. Char containing coal ash, Cab-O-Sil, and unreacted carbonaceous material is collected in a char pot. The yields of individual carbon-containing products are reported as percent of carbon contained in the feed coal.

RESULTS AND DISCUSSION

The product distributions from pyrolysis of coal in nonreactive gaseous atmospheres of helium, nitrogen, and argon were obtained as a function of temperature, residence time, and pressure (Steinberg, 1983). A specific purpose of this work was to find whether the heat transfer characteristics of these gases had any influence on the pyrolytic product distribution and if so, to what extent.

The yield versus coal particle residence time curves for various products obtained from the flash pyrolysis of New Mexico subbituminous coal in helium are shown in Figure 2 for different isothermal temperatures, from 700° to 1000°C. Although the total carbon conversion to hydrocarbon gases, BTX, and CO_x tends to increase with coal particle residence time, one may note that most of the conversion occurs within 1 sec, and further increase in residence time does not cause significant increase in total carbon conversion. For instance, at 800°C, a carbon conversion equivalent to 10% is achieved at 1 sec and increasing the residence time by 0.6 sec increases the total carbon conversion by only 1.6%.

This is expected because the hydrogen required for stabilization of free radicals generated from coal and from pyrolysis tar is "donated" by coal itself, and the amount of "donatable" hydrogen, present mostly in the hydroaromatic rings in coal, is a fixed quantity. The extent of cracking of hydroaromatic rings to release hydrogen is probably not influenced by coal particle residence time alone. The hydroaromatic rings are connected to other units and functional groups in coal by chemical bonds of different strengths. As the temperature is increased, bonds with higher dissociation energy are thermally broken and additional hydrogen can be released from the hydroaromatic portion of coal. Initial acceleration in the reaction rate, especially during the early stages of pyrolysis, has been attributed to the occurrence of simultaneous reactions and/or to the resistance of intraparticle mass transfer (Kobayashi, 1977).

The product curves show that ultimate asymptotic yields have been obtained for methane and CO_x within the residence time employed. The production characteristic of ethylene appears to be considerably different from that of methane and CO_x. Polymethylene moieties present in coal are considered to be main precursors for ethylene production (Calkins, 1983). At low temperatures, ethylene is produced only at long residence times. (Similar behavior is noticed in CO_x production.) At higher temperatures, ethylene is continuously produced throughout the length of the reactor and no maximum in its yield is visible from the curves. Extrapolation of the 900°C curve indicates a maximum of about 5.8% at about 2-sec coal particle residence time. At temperatures above 900°C, ethylene undergoes decomposition as can be clearly seen in Figure 3 in which the product yields are plotted as a function of temperature for various residence times. Because of lack of hydrogen, only part of the decomposed ethylene results in the formation of methane. It is seen from this Figure that at 1.5 sec ethylene yield decreases from 4.9% at 900°C to 2.3% at 1000°C (a reduction of 2.6% in absolute yield), whereas methane yield increases from 3.4% at 900°C to 5.0% at 1000°C (1.6% increase in absolute yield). The increase in the BTX yield from 1.5% at 900°C to 2.2% at 1000°C (Table 3) might be attributed to the secondary reactions of ethylene unaccounted for as above.

It appears that cracking of polymethylene groups is catalyzed by in situ mineral matter in coal. When an acid-treated New Mexico subbituminous coal containing 6.2% ash was pyrolyzed, ethylene yields

were 25 to 30% lower than those from original coal containing 22.8% ash. An increase in the temperature from 900° to 1000°C decreased the ethylene yields by approximately 50% in both cases (Table 3). The presence of coal mineral matter, however, seems to favor the formation of methane and BTX at the expense of ethylene. For example, in the case of untreated coal, the combined yields of methane and BTX increase by 2.3% C against a 2.6% decrease in the yield of ethylene. On the other hand, in the case of acid-treated coal, ethylene formed at low temperature seems to undergo secondary thermal cracking reactions at high temperature resulting in the formation of char.

As can be seen in Table 3, reduction of cationic content of coal by acid treatment increased the yields of CO and CO₂ gases. The decrease in ethylene and BTX yields were more than compensated by increase in CO_x yield in that the overall carbon conversion to hydrocarbon gases plus BTX and CO_x actually increased. From studies based on model compounds (Cypres, 1975) and coal (Schafer, 1979), it is known that phenolic functional groups in coal are mainly responsible for the production of CO. On this basis, it is suggested that coal mineral matter might catalyze the polymerization reactions involving phenolic groups or their precursors during early stages of devolatilization, thereby inhibiting the evolution of CO. In situ mineral matter seems to catalyze the dimerization of solvent radicals under coal liquefaction conditions (Sundaram, 1983-1); caution should, however, be exercised in extending these results to coal pyrolysis because of drastic changes in reaction severity.

In addition, it is also possible that the acid treatment could have caused changes in pore structure and/or chemical structure of coal, which may have influenced the pyrolysis behavior. A more thorough and systematic study is required before an acceptable mechanism can be advanced.

In any case, the preliminary results from the present study are different from recent findings by Franklin of MIT (Franklin, 1981) who pyrolyzed coal via an extensively used captive sample technique with reported heating rates of about 1000°K/sec and holding times up to 5 sec. In the later study, an acid-demineralized Pittsburgh No. 8 coal was spiked with various inorganic additives such as calcite, quartz, kaolinite, montmorillonite, etc., and calcium minerals were found to be particularly effective in cracking oxygen functional groups to produce CO. It is not clear whether the differences between the two studies are due to their experimental techniques (BNL: entrained flow, short residence time, high heating rate; MIT: captive sample, long holding time, slow heating rate) or to coal rank (BNL: subbituminous coal; MIT: bituminous coal). We intend to pursue this subject matter in more detail in the future.

The results of pyrolysis experiments in other nonreactive gases are shown in Figure 4. The total conversion includes the yields of methane, ethylene, BTX, and CO_x. Because of analytical limitations in measuring CO in the presence of nitrogen or argon, CO yield data from helium pyrolysis experiments were used to determine total conversion under nitrogen and argon atmospheres. Examination of Figure 4 with

this assumption suggests that the total carbon conversion is almost unaffected by pyrolysis atmosphere under the conditions reported. An increase in total conversion in the order of $\text{He} > \text{N}_2 > \text{Ar}$ was reported earlier (Sundaram, 1983-2). In that study, coal was pyrolyzed at a higher pressure (200 psi) and the results obtained from experiments employing somewhat nonuniform residence time conditions (3.5 to 4.7 sec) were compared, whereas in this paper results from more uniform, narrow range residence time (1.5 to 1.7 sec) experiments are compared. Pyrolysis experiments under other conditions are in progress, and the results will be published in a future report.

Even though the total carbon conversion remained almost unaffected by pyrolysis atmosphere, the relative yields of pyrolysis products seem to be altered by different nonreactive gases. A clear-cut trend in product yields, however, is not revealed in Figure 4. Nevertheless, some generalizations on product yields could be made. Conversion to methane followed the increasing order of $\text{He} > 50\% \text{He}/50\% \text{Ar} > \text{N}_2 > \text{Ar}$. The yield of ethylene was lower in helium atmosphere than in N_2 or Ar and the ethylene yield maximized at 900°C in all gaseous atmospheres. A slightly larger amount of BTX was produced in Ar and He/Ar than in He or N_2 up to 900°C; at 1000°C, the BTX yield is almost the same in all gaseous atmospheres.

The gas-film heat transfer coefficient and hence the heat-up rate of the coal particles were found to follow the order $\text{He} > \text{N}_2 > \text{Ar}$. It appears that the magnitude of difference in the particle heat-up rate is not large enough to significantly affect the total volatiles yield under the conditions reported herein. The effect of nonreactive gases on the physical and chemical characteristics of the resulting char is not known at present. In one investigation, the surface area of pyrolysis char was found to be affected by the pyrolysis atmosphere and it was reported to follow the order, $\text{He} > \text{Ar} > \text{N}_2$ though for unexplained reasons (Thakur, 1982).

CONCLUSIONS

When a New Mexico subbituminous coal was pyrolyzed in different nonreactive gases, the relative yields of volatile products were altered but the total carbon conversion remained almost unaffected. Acid treatment of the coal enhanced the production of CO_x gases but inhibited the formation of ethylene. This suggests that the in situ mineral matter might catalyze polymerization reactions involving oxygen functionalities in coal.

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TABLE 1. ANALYTICAL DATA FOR NEW MEXICO SUB-BITUMINOUS COAL

Ultimate Analysis	(wt % dry)	Ultimate Analysis	(dry)
Carbon	: 55.9	Volatile Matter	: 34.9
Hydrogen	: 4.3	Fixed Carbon	: 42.4
Nitrogen	: 1.1	Ash	: 22.8
Sulfur	: 1.0		
Oxygen (by diff.)	: 14.9		

TABLE 2. PHYSICAL PROPERTIES OF GASES AT 900°C AND ATM. PRESSURE

	Helium	Nitrogen	Argon
ρ_g (gm/cc)	2.80×10^{-3}	1.96×10^{-2}	2.81×10^{-2}
μ_g (CPS)	5.78×10^{-2}	5.56×10^{-2}	7.29×10^{-2}
K_g (Cal/cm ² °K sec)	9.78×10^{-4}	1.68×10^{-4}	1.13×10^{-4}
C_p (Cal/Mole °K)	7.57	4.97	4.97

TABLE 3. FLASH PYROLYSIS OF NEW MEXICO SUB-BITUMINOUS COAL IN HELIUM ATMOSPHERE AT 50 PSI TOTAL PRESSURE

Particle Residence Time : 1.3 - 1.5 sec.

Percent Carbon Conversion to Designated Products

Run No.	Untreated Coal*		Acid-Washed Coal**	
	756	754	770	770
Temperature, °C	900	1000	900	1000
<u>Product Yields:</u>				
CH ₄	3.4	5.0	3.7	3.8
C ₂ H ₄	4.9	2.3	3.4	1.7
BTX	1.5	2.2	2.4	1.9
CO	2.7	5.6	5.8	8.1
CO ₂	1.1	1.8	2.0	2.5
Total	13.6	16.9	17.3	18.0

* Ash Content: 22.8%

** Ash Content: 6.2%

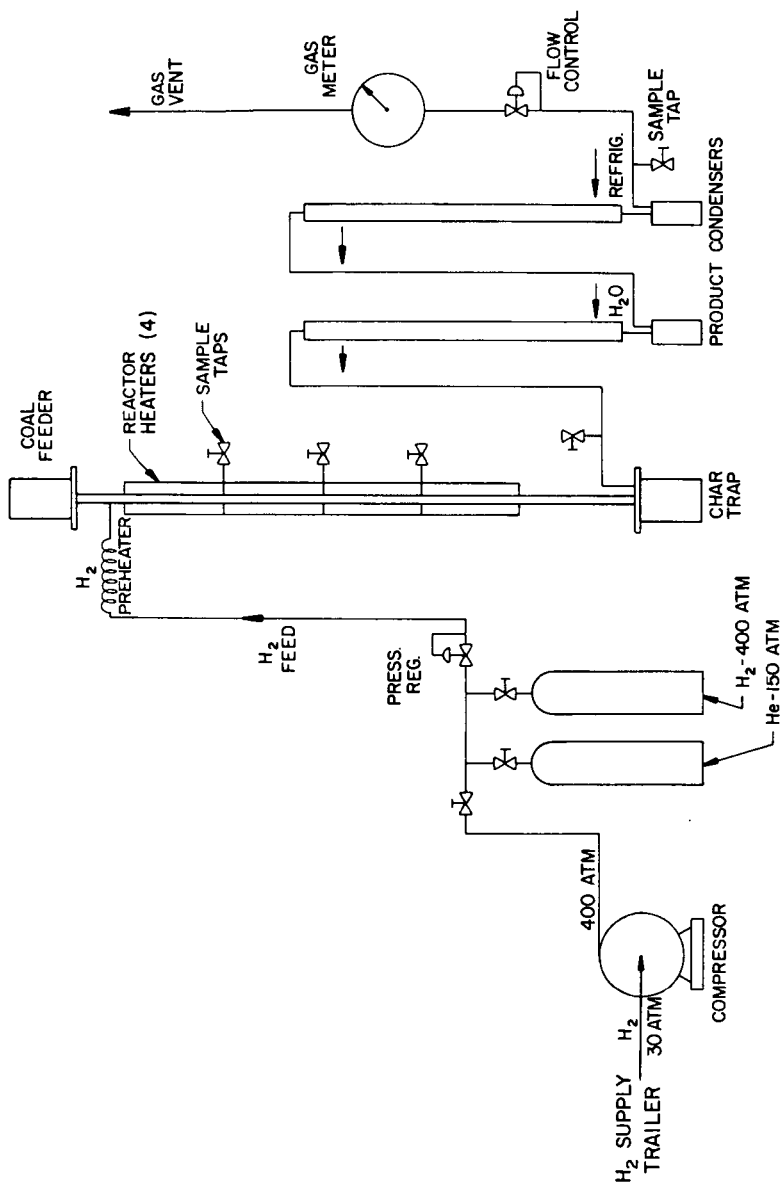


Figure 1. Schematic Representation of Pyrolysis Reactor.

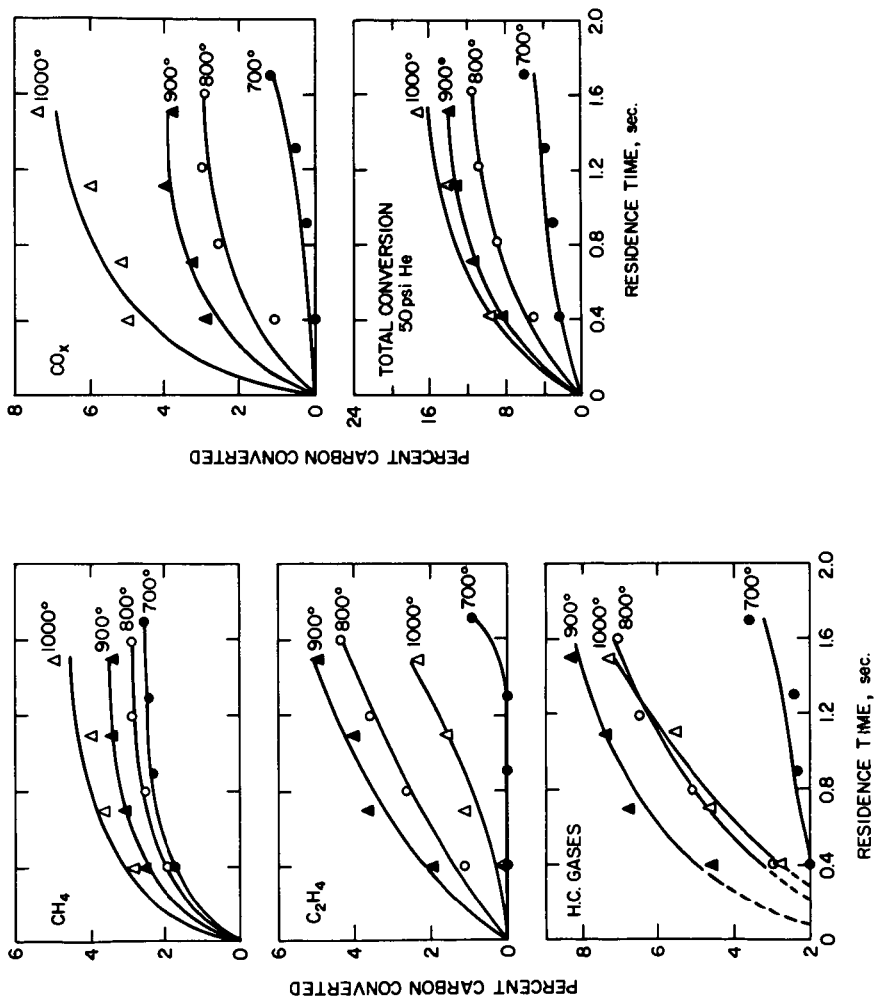


Figure 2. Flash Pyrolysis of New Mexico Sub-Bituminous Coal in Helium. Effect of Coal Particle Residence Time on Product Yields.

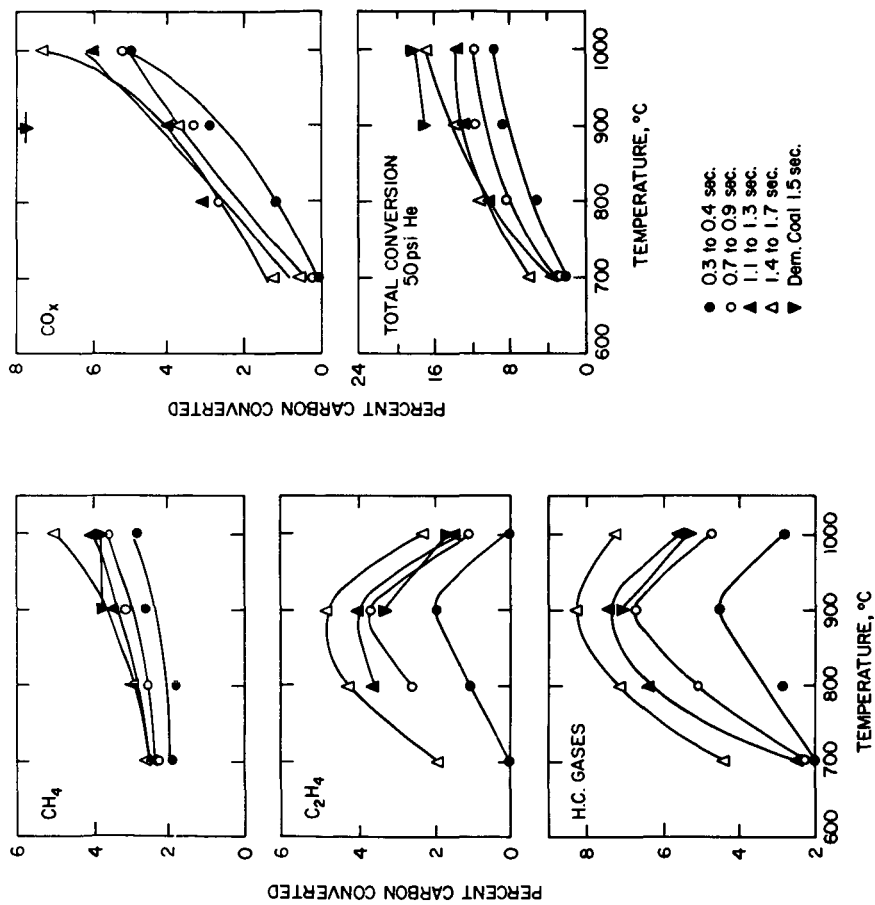


Figure 3. Flash Pyrolysis of New Mexico Sub-Bituminous Coal in Helium. Effect of Coal Temperature on Product Yields.

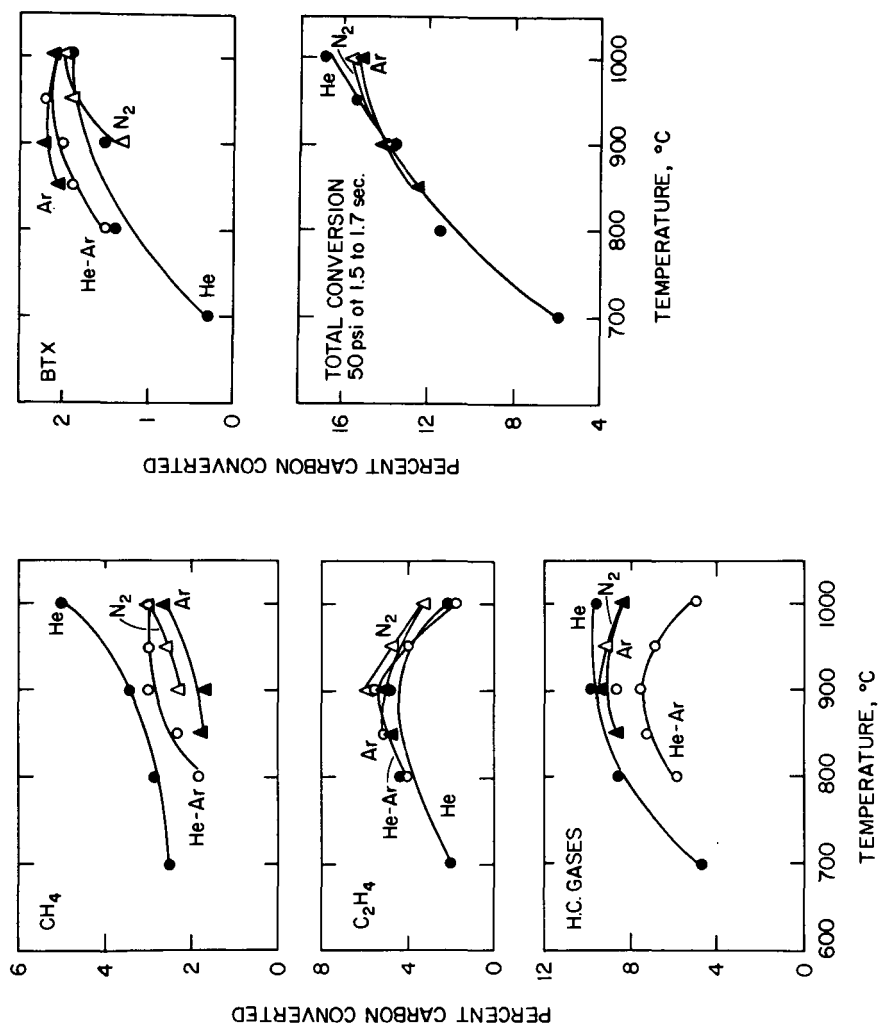


Figure 4. Flash Pyrolysis of New Mexico Sub-Bituminous Coal in He, N₂, and Ar. Effect of Temperature on Product Yields.